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(54) Title: AQUEOUS CEMENT COMPOSITION

(57) Abstract: A fresh aqueous cement composition suitable for building purposes is described. It contains, besides a hydraulic cement, a methyl ethyl cellulose ether having a DS methyl of 0.4-2.2, a DS ethyl of 0.05-0.8 and a MS hydroxy- (C_2-C_3)- alkyl of 0-2. The cellulose ether imparts excellent rheology properties, including a high water-retention combined with a long open time, to the cement composition. A dry blend and a rheology additive containing the cellulose ether are also described.

AQUEOUS CEMENT COMPOSITION

The present invention relates to a fresh aqueous cement composition suitable for building purposes. It contains a methyl ethyl cellulose ether, which imparts excellent rheology properties, including a high water-retention combined with a long open time, to the cement composition.

Non-ionic cellulose ethers, such as methyl cellulose ethers, methyl hydroxyethyl cellulose ethers and methyl hydroxypropyl cellulose ethers, are frequently used in fresh cement mortars as a water-retention and thickening agent. The methyl cellulose ethers also improve such rheology properties as workability, stability and adhesion. Other commercially available cellulose ethers for modern cement-based compositions are ethyl hydroxethyl cellulose ethers. It is also well known to combine the cellulose ethers with synthetic polymers, e.g. polyacrylamides and polyvinyl alcohols, in order to further improve the properties of the fresh cement mortars. See for example US 5 234 968.

It is also of essential importance that the fresh cement composition has an open time necessary for the work to be done in a practical manner and a satisfactory adhesion and that the fresh cement composition, after curing, results in a product of good strength.

According to the present invention it has now been found that a fresh, aqueous cement composition containing a hydraulic cement and a methyl ethyl cellulose ether, having a DS methyl of 0.4-2.2, preferably 0.6-1.8; a DS ethyl of 0.05-0.8, preferably 0.1-0.5; and a hydroxy-(C_2-C_3)-alkyl of 0-2, preferably 0.1-1.2; exhibits good rheology properties, such as a high water-retention combined with a long open time, a good adhesion and a high strength of the cured product. The amount of the methyl ethyl cellulose ether is suitably from 0.05-3%, preferably 0.1-2%, and most preferably from 0.2-1.0, by weight of the dry weight of the fresh cement composition.

The methyl ethyl cellulose ether has advantageously a flocculation temperature between 55°C and 85°C, preferably between 60°C and 80°C, while the viscosity suitably is between 200 mPa·s and 20000 mPa·s, measured in a 1% by weight solution at 20°C according to Brookfield LV, spindle 1-4, 12 rpm.

The presence of both methyl and ethyl groups in the cellulose ether prolongs the open time of the fresh cement composition that is available without undue degree of reduction of the adhesion and the strength of the cured product. The presence of hydroxyethyl or hydroxypropyl groups does not suppress but normally improves these properties further. In addition, the use of the cellulose ether in question in the cement composition results in an air entrainment that supports an excellent consistency of the fresh cement composition and a good resistency towards formation of cracks in the cured product. The cement composition of the invention has properties, which make them suitable to be used as a cement mortar, such as plaster, joint fillers, floor screeds, grouts, and tile adhesives.

The methyl ethyl cellulose ether disclosed can be produced by reacting an alkali cellulose with methyl chloride, ethyl chloride and optionally ethylene oxide and/or propylene oxide. Suitably the reaction is performed in the presence of an inert organic reaction medium at temperatures between 60-115°C in accordance with the principles disclosed in the textbook: Ullmann´s Encyclopaedia of Industrial Chemistry, Fifth, Completely Revised Edition Volume A5, p 468-474.

According to the invention, the hydraulic cement can be ordinary Portland cement, low heat Portland cement, white Portland cement, rapid hardening Portland cement, and aluminous cement, or mixtures thereof. Suitably the hydraulic cement contains 75-100% by weight of ordinary Portland cement or white Portland cement. The hydraulic cement can also be

combined with 0-25% by weight of lime and/or gypsum. In general, the cement composition also contains fillers, although for certain applications, such as cement glue for mosaic, the presence of fillers may not be required or desired. The fillers are usually an inorganic material with a particle size of 5 mm or less. The inorganic material is preferably selected from the group consisting of silica, calciumcarbonate, different types of dolomite and expanded minerals. The fillers for use in plasters suitably comprise at least 98% by weight of particles having a particle size less than 4 mm, while fillers for tile adhesives, grouts, joint fillers and floor screeds normally comprise at least 98% by weight of particles having a particle size less than 1.5 mm.

According to the invention the cement composition can, besides the methyl ethyl cellulose ether, also contain other additives which affect the rheology. Examples of such other additives are other polymers consisting of water-soluble or water-dispersable synthetic organic polymers resistant to alkali, such as polyvinyl-acetates, polyvinyl alcohols, polyacrylamides, copolymers between vinyl acetate and vinyl alcohol, copolymers between vinyl acetate, vinyl chloride and vinyl laurate, copolymers between acrylates and methyl methacrylates, anionic or nonionic starch derivates, polymeric plasticizers and mixtures thereof; and clays, such as kaolin, bentonite, attapulgite and mixtures thereof. These additives have normally a thickening effect and improve the stability of the fresh cement composition and the flexibility of the cured product, thereby reducing the risk of crack formation. A suitable rheology additive for use in a fresh composition according to the invention comprises 10-100%, preferably 40-90% by weight of a methyl ethyl cellulose ether according to the invention, 0-90%, preferably 10-60% by weight of another polymer consisting of water-soluble or

water-dispersible synthetic organic polymer resistant to alkali, and 0-90%, preferably 0-50% by weight of clay.

In addition to the above mentioned components the cement composition can also contain a number of other ingredients, such as air-entraining agents, retarders, accelerators, nonpolymeric plasticizers, pigments, colorants and corrosion inhibitors.

A typical fresh cement composition according to the invention contains 0.05-3%, preferably 0.1-2% and most preferably 0.2-1%, by dry weight of the composition of a rheology additive containing a methyl ethyl cellulose ether as defined above,

8-99.5, preferably 12-65% by dry weight of the composition of a hydraulic cement,

0-91, preferably 45-83% by dry weight of the composition of a filler having a particle size of 5 mm or less,

0-10, preferably 0.05-4% by dry weight of the composition of other ingredients, and

10-60, preferably 15-40% by weight of the fresh cement composition of water.

The fresh composition may be prepared by first mixing at least a part of the cement with the rheology additive and the other ingredients, whereupon the remaining cement and the filler is added in one or more steps and thoroughly mixed to a homogeneous dry blend. Just before the actual use of the fresh cement composition a suitable amount of the dry blend is thoroughly mixed with the desired amount of water.

The present invention is further illustrated in the following examples.

Example 1

Five cement compositions suitable to be used as a tile fix mortar were prepared by mixing according to DIN 18156, 400 g of ordinary Portland cement; 525 g of sand having a particle size of less and 0.5 mm and 75 g of siliceous fluor having a particle size of less than 0.5 mm as a filler; 4 g

of any one of the nonionic cellulose ethers according to Table 1 below; and 235 g of water.

Table I. Nonionic cellulose ethers used in the compositions

	Compositions				
Property	**1**	**2**	**A**	**B**	**C**
DS methyl	1.35	1.35	1.5	1.5	1.6
DS ethyl	0.12	0.12	0	0	0
MS hydroxyethyl	0.12	0.06	0.12	0.06	0
MS hydroxypropyl	0	0	0	0	0.2
Viscosity [1], mPa·s	7830	11800	11500	12400	3720
Flocculation temperature, °C	69	67	68	68	61

[1]Viscosity measured according to Brookfield LV, spindle 1-4, 12 rpm in 1% by weight solution at 20°C

The properties of the cement composition were examined with regard to air content (by density measurements), flow table value (ASTM C280-68), slip ($UEAT_c$), open time measured as tensile strength on non-vitreous tiles (DIN 18156, part 2). The tiles were applied after 0.5 and 10 minutes and the tensile strength measured after 28 days. The results obtained are shown in Table II below.

Table II. Performance of the cement compositions

	Compositions				
Property	**1**	**2**	**A**	**B**	**C**
Air content, %	15.0	14.1	14.5	13.7	15.8
Flow table value, mm	160	159	158	157	167
Slip, mm	1	1	2	2	1

Open time as tensile strength, kg/cm^2					
0 min	24.8	23.8	24.6	13.9	22.6
5 min	18.1	20.2	10.5	9.8	15.7
10 min	12.0	10.8	7.8	8.1	7.1

From the results it is evident that the open times during which a high tensile strength are obtainable is essential longer for the cement compositions 1 and 2 according to the invention than for the comparison compositions A, B and C.

Example 2

Three cement compositions were prepared according to the formula in Example 1 but the amount of water was increased to 240 g. The nonionic cellulose ethers exhibited the following properties.

Table III. Nonionic cellulose ethers used in the cement compositions

	Compositions		
Property	**3**	**4**	**D**
DS methyl	1.2	1.5	1.8
DS ethyl	0.25	0.25	0
MS hydroxyethyl	0.12	0.12	0.12
Viscosity, mPa·s	16900	17700	18900
Flocculation temperature, °C	64.5	61.7	64.6

The properties of the cement compositions were examined in the same manner as in Example 1, but with the exception that the air content was not measured. The following results were obtained.

Table IV. Performance of the cement compositions

	Compositions		
Property	**3**	**4**	**D**
Flow table value, mm	141	140	138
Slip, mm	2	3	2
Open time as tensile strength, kg/cm^2			
0 min	21.7	25.8	21.9
5 min	17.1	23.8	9.8
10 min	7.6	5.4	0.8

The compositions 3 and 4 according to the invention exhibited essential better open times than the comparison composition D.

Example 3

Two cement compositions were prepared in accordance with Example 1, but the water content was adjusted so the cement compositions received a slip between 0.5 mm and 1 mm. Furthermore, two similar cement compositions were prepared. The difference was that these compositions as a rheology additive contained a blend of 4 g of any of the cellulose ethers and 0.08 g of a polyacrylamide. The rheology additive used in the four cement compositions are shown in Table V.

Table V. Rheology additive used in the compositions

	Compositions			
Components	**6**	**7**	**E**	**F**
Cellulose ether, g	4	4	4	4
DS methyl	0.9	0.9	-	-
DS ethyl	0.35	0.35	0.95	0.95
MS hydroxyethyl	0.9	0.9	2.35	2.35
Viscosity, cP	2100	2100	6000	6000
Flocculation, °C	70.1	70.1	69	69
Polyacrylamide, g	-	0.08	-	0.08

The air content, slip, flow table value and open time of the four cement compositions were determined in the same manner as in Example 1. Furthermore, the water-retention was determined according to ASTM C91-71 (modified with a funnel diameter of 80 mm and an evacuation for 10 minutes). The following results were obtained.

Table VI. Performance of the cement compositions

	Compositions			
Property	**6**	**7**	**E**	**F**
Water addition, g	220	250	225	255
Air content, %	24	20	22	23
Flow table value, mm	158	164	154	154
Slip, mm	1	0.5	1	0.5
Open time as tensile strength, kg/cm^2				
0 min	21.8	21.1	12.7	12.0
5 min	16.6	12.7	10.6	6.0
10 min	7.2	6.5	4.3	0.0
Water retention, %	97.1	96.7	97.2	96.1

The cement compositions 6 and 7 according to the invention have essentially better open time property than the comparisons E and F. Water-retention values between 94% and 98% are excellent.

CLAIMS

1. A fresh aqueous cement composition containing a hydraulic cement and a cellulose ether **characterised in that** the composition contains a methyl ethyl cellulose ether having a DS methyl of 0.4-2.2, a DS ethyl of 0.05-0.8 and a MS hydroxy-(C_2-C_3)-alkyl of 0-2.

2. A cement composition, according to claim 1, **characterised in that** the methyl ethyl cellulose ether has a DS methyl of 0.6-1.8, a DS ethyl of 0.1-0.5 and a MS hydroxy-(C_2-C_3)-alkyl of 0.1-1.2.

3. A cement composition according to claim 2, **characterised in that** the hydroxyalkyl group is hydroxyethyl.

4. A cement composition according to claim 2, **characterised in that** the hydroxyalkyl is hydroxypropyl.

5. A cement composition according to claims 1-4, **characterised in that** it contains 0.05-3% by weight of the methyl ethyl cellulose ether.

6. A cement composition according to any one of claims 1-5, **characterised in that** it contains 0.05-3% by dry weight of a methyl ethyl cellulose ether as defined in claims 1-4, 8-99.5% by dry weight of the composition of a hydraulic cement, 0-91% by dry weight of the composition of a filler having a particle size of 5 mm or less, 0-10% by dry weight of the composition of other ingredients, and 10-60% by weight of the composition of water.

7. A cement composition according to claim 6, **characterised in that** it contains 0.1-2% by dry weight of a methyl ethyl cellulose ether as defined in claims 1-4, 12-65% by dry weight of the composition of a hydraulic cement, 45-83% by dry weight of the composition of a filler having a particle size of 5 mm or less, 0.05-4% by dry weight of the composition of other ingredients, and 15-40% by weight of the composition of water.

8. A dry blend, suitable for use in the preparation of the fresh cement composition according to claim 1-7, **characterised in that** contains 0.05-3% by dry weight of a methyl ethyl cellulose ether as defined in claims 1-4, 8-99.5% by dry weight of the composition of a hydraulic cement, 0-91% by dry weight of the composition with a filler having a particle size of 5 mm or less, and 0-10% by dry weight of the composition of other ingredients.

9. A dry blend according to claim 7, **characterised in that** it contains 0.1-2%, by dry weight of a methyl ethyl cellulose ether as defined in claims 1-4, 12-65% by dry weight of the composition of a hydraulic cement, 45-83% by dry weight of the composition of a filler having a particle size of 5 mm or less, and 0.05-4% by dry weight of the composition of other ingredients.

10. A rheology additive suitable for use in a fresh cement composition or dry blend according to claim 1-8, **characterised in that** it contains 40-98.5% by dry weight of a methyl ethyl cellulose ether as defined in claims 1-4, 1.5-60% by weight of another polymer consisting of a water-soluble or water-dispersible synthetic organic polymer resistant to alkali, and 0-50% by weight of clay.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 02/02164

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C04B 24/38, C08L 1/28, C04B 28/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C04B, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WPI/Derwent's abstract, Accession Number 2000-658302, week 200064, ABSTRACT OF JP, 2000203915, A, (SHINETSU CHEM IND CO LTD), 25 July 2000 (25.07.2000) --	1-10
A	US 5372642 A (UWE BARTZ ET AL), 13 December 1994 (13.12.94), abstract --	1-10
A	FR 2709122 A1 (SOGEA-FR.), 24 February 1995 (24.02.95), abstract --	1-10

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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